

# (12) UK Patent Application (19) GB (11) 2 277 324 (13) A

(43) Date of A Publication 26.10.1994

(21) Application No 9407646.0

(22) Date of Filing 18.04.1994

(30) Priority Data

(31) 4312973 (32) 21.04.1993 (33) DE

(71) Applicant(s)

**Basf Aktiengesellschaft**

**(Incorporated in the Federal Republic of Germany)**

**D-67056 Ludwigshafen, Federal Republic of Germany**

(72) Inventor(s)

**Hans-Josef Sterzel**

**Heinz Ruetter**

**Harald Dauns**

**Hans Georg Matthies**

**Roland Minges**

(74) Agent and/or Address for Service

**J Y & G W Johnson**

**Furnival House, 14-18 High Holborn, LONDON,**

**WC1V 6DE, United Kingdom**

(51) INT CL<sup>5</sup>

**C08G 63/08**

(52) UK CL (Edition M )

**C3R RPX R37N1**

**U1S S1814 S3002**

(56) Documents Cited

**GB 2246573 A US 5270400 A US 4800219 A**

(58) Field of Search

**UK CL (Edition M ) C3R**

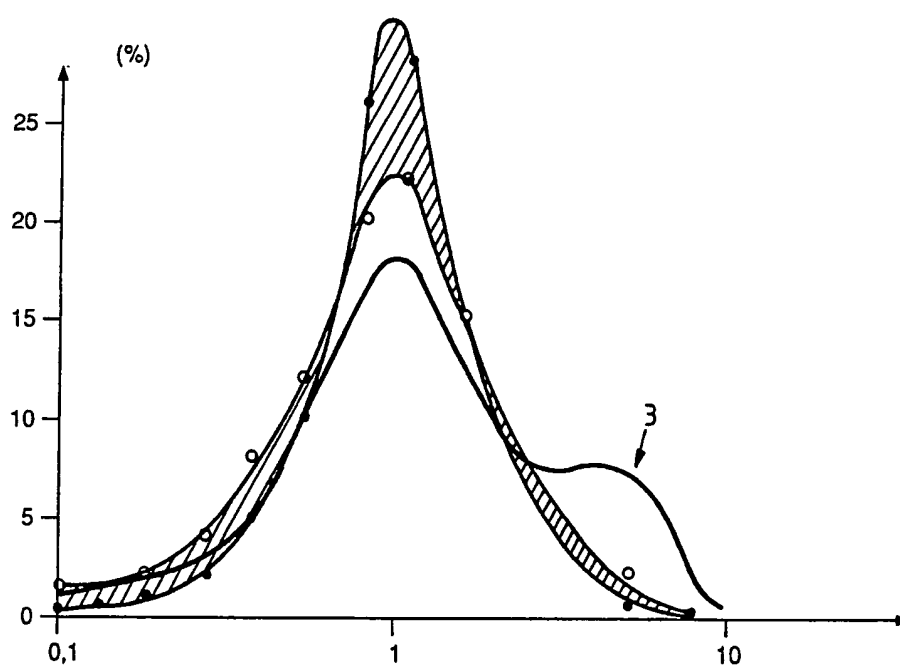
**INT CL<sup>5</sup> C08G**

**Online databases : WPI**

(54) **Polyactide having a broadened molecular weight distribution**

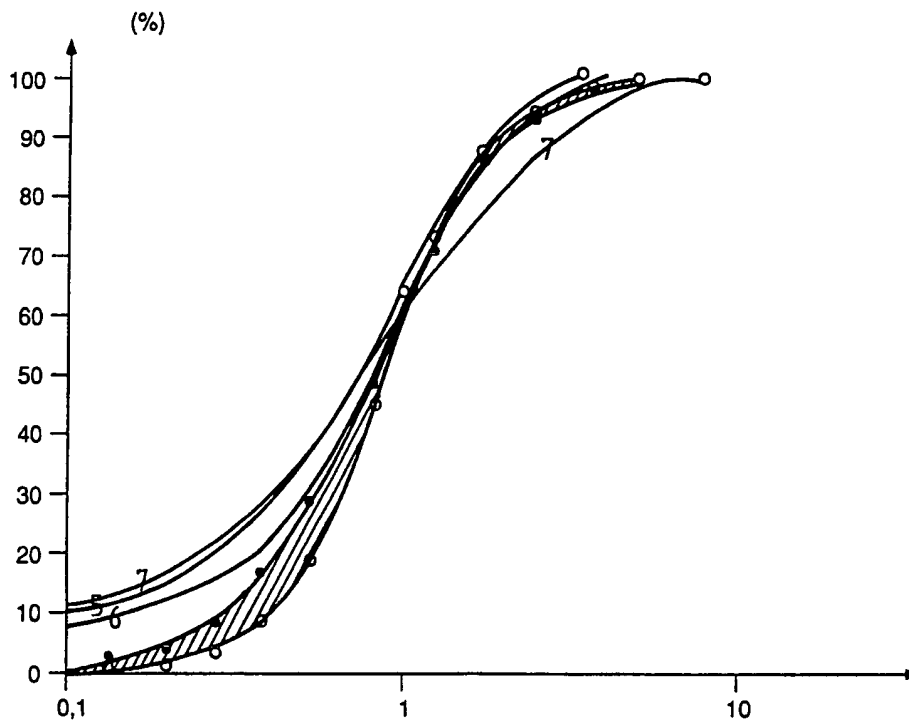
(57) A polylactide is provided having a number average molecular weight of greater than 30,000 or a weight average molecular weight of greater than 60,000, wherein the proportion by weight in the molecular weight range up to 10,000 and in the molecular weight range above 500,000 is in each case from 5 to 15%. The polylactide may be prepared either by adding initiator during the production of the polymer in a plurality of portions at different times and/or at a plurality of locations if the process is carried out continuously or by using both a monofunctional initiator and a polyfunctional initiator or by carrying out the polymerisation in a continuous stirred reactor.

FIG.1



2/2

FIG.2



Poly lactide having a broadened molecular weight distribution

#### Description

5 Poly lactide is prepared by ring-opening polymerization of lactide with retention of the configuration. Poly-L- and poly-D-lactide can be obtained under appropriate processing conditions, specifically by being briefly maintained at from 100 to 120°C, as par-  
10 tially crystalline polymers having a glass transition temperature of from 50 to 55°C and a crystallite melting point of around 175°C. Admixing of DL- or DD-lactide with L-lactide or of DL- or LL-lactide with D-lactide gives copolymers having a reduced rate of crystallization and a reduced crystalline content: the melting  
15 point drops, but the glass transition temperature is maintained. If, however, it is desired to reduce the glass transition temperature, a copolymerization with glycolide, which is cyclic, is carried out. Homopolymeric polyglycolide has a glass transition temperature of from 20 to 25°C. Copolymerization of appropriate  
20 proportions of lactide and glycolide accordingly allow the glass transition temperature to be set at between about 20 and 55°C.

The glass transition temperature of poly lactide plays an important part in composting of the polymer and in its absorption by  
25 body tissues. The reason for this is that degradation of the material takes place in the first step by nonspecific hydrolysis of the polyester chains. In the second step, the resultant lactic acid is degraded by microorganisms or enzymatically. The rate - determining step is the nonspecific hydrolysis of the ester,  
30 which depends on the glass transition temperature of the polymer; it is a factor of about 100 faster at from 5 to 10°C above the glass transition temperature than at from 5 to 10°C below it.

The degradation rate can thus be matched to requirements by fixing  
35 the glass transition temperature. Depending on whether fast or slow absorption by living human tissue is required, copolymers of lactide and glycolide having a glass transition temperature below or above 37°C are employed.

40 Poly lactide, specifically homopolymeric poly lactide, is also increasingly attracting interest as a rottable packaging material. The essential point here is that the temperature in fast composting systems is generally above 50°C for an extended period. pH values above 7 also significantly accelerate hydrolysis.

For the production of moldings or packaging systems such as films, bottles, thermoformed tubs or injection-molded articles, the solid polymers must be melted and the melts forced through dies into molds or shaped to give films. To this end, the melt must be highly flowable. According to a proposal not published before the priority date of the present application, crystallization can be promoted by stretching during solidification and a viscosity of greater than 3000 N/mm<sup>2</sup> is thus achieved.

10 To this end, the material must have very high melt viscosity in the processing region between the glass transition temperature and the crystallite melting point, and the melt viscosity must be highly independent of changes in temperature. This is important since the heat liberated during orientation and crystallization, 15 which does not take more than a few seconds, can only be dissipated poorly; experience has shown that the material warms by up to 35°C, with the consequence, for example, that uneven shaping occurs during stretch blow molding.

20 Uniform blow molding thus requires a low dependence of the melt viscosity on the temperature, otherwise the temperature increase would cause a rapid drop in melt viscosity at a point of locally increased stretching and would thus cause overstretching at this point.

25 The known polylactide molding compositions cause problems in processing due to their inadequate melt viscosity.

The melt viscosity can be modified per se through the molecular 30 weight distribution, with the following prerequisite:

Polyglycolide and polylactide are obtained by ring-opening bulk polymerization initiated by metal alkoxides or metal carboxylates, giving polymers having a narrow molecular weight distribution. 35 tion.

The originally narrow molecular weight distribution is broadened by transesterification reactions during the polymerization. Thus, US Patent 4,719,246 describes the transesterification between two 40 polylactides comprising different enantiomers. After a number of heating and cooling cycles taking from 10 to 60 minutes, a random distribution of chain units in the previously separate polymers is observed. However, the proportion of, in particular, low-molecular-weight units should be higher, and the process of subsequent transesterification also takes too long to be economic. 45

It is an object of the present invention to prepare lactide polymers having good processing properties in the above sense.

We have found that this object is achieved by engineering measures and novel initiators which allow the synthesis of polylactide which contains sufficient low-molecular-weight units to develop an advantageous lubricating action during processing and which, on the other hand, contains sufficient relatively high-molecular-weight units to achieve a low dependence of the melt viscosity on the temperature. Molecular weight averages as hereinafter contemplated are by number ( $\bar{M}_n$ ).

Polylactides having a relatively broad molecular weight distribution in the sense of the invention can be prepared according to the invention as follows:

The polymerization is carried out in a continuous stirred reactor. Monomer (lactide) and initiator are fed continuously to the reactor, and the corresponding product stream is discharged continuously (Fig. 3). In this variant, preference is given to the preparation of high proportions by weight of relatively low molecular weights down as far as the monomer.

If very low degrees of polymerization are undesired, their proportion can be reduced by modifying this process: the polymerization is carried out in part in a continuous stirred reactor, downstream of which is a reactor with plug flow. This reactor can be a flow tube or a forced conveying apparatus. The molecular weight distribution can be further modified by metering further initiator into the reactor with plug flow before the point of entry of the polymerizing material, which results in a shortened reaction time in overall terms or a shift in the mean molecular weight to lower values.

A similar residence-time spectrum is also achieved by metering the monomer and the initiator into a continuous reactor with plug flow, downstream of which is a branch line which allows a freely selectable proportion of the polymerizing material to be recycled to the inlet and the remainder to be conveyed into a downstream, second reactor with plug flow. A further initiator can likewise be metered into the inlet of this reactor. In this way, the conversion in the back-mixed reaction space can be controlled.

The more material recycled after the first reactor to its inlet in relation to the material fed to the second reactor, the higher the proportion of polylactide having a low degree of polymerization. This ratio is simple to control and thus allows

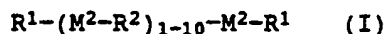
molecular weight distributions to be established in a targeted manner.

The polymerization temperature is from 180 to 210°C, and the overall residence time is from 15 to 60 minutes, with a total of from  $10^{-6}$  to  $10^{-3}$  mol, preferably from  $10^{-5}$  to  $10^{-4}$  mol, of initiator being employed per mole of monomer.

The novel process preferably allows the preparation of polylactide having an increased low-molecular-weight content. However, it is also possible to prepare polylactides having increased low-molecular-weight contents in the case of polymerization in a stirred batch reactor or in a flow tube. In this case, not all the initiator is added, as usual, at the beginning of the polymerization, but instead the initiator is divided into portions and metered in at a plurality of points in time distributed over the process (at a plurality of consecutive locations in the case of a flow tube). This means that new chains are started on each fresh addition, and a molecular weight distribution in which the lower molecular weights are predominant is obtained.

The proportion of material having an increased degree of polymerization for increasing the melt viscosity can be modified by, in accordance with a proposal not published before the priority date of the present application, carrying out the polymerization in the presence of not only monofunctional initiators, but also in the presence of polyfunctional initiators. For the same growth rate of the initiating centers, the chain started by a bifunctional initiator grows twice as fast as the chain started by a monofunctional initiator.

The corresponding situation applies for higher-functional initiators. Polyfunctional initiators for the polymerization of lactides are essentially chain-form or branched metal alkoxides or metal carboxylates of the structure I, II or III:



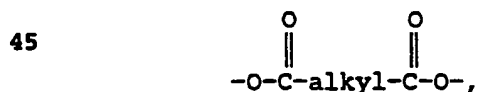
where

$M^2$  is a divalent metal, such as Sn(II), Zn or Mn,

$R^1$  is alkoxy or carboxyl, and

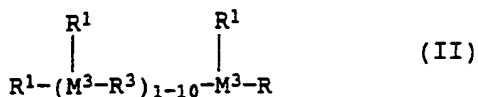
$R^2$  is  $-O-(CH_2)_n-O-$ , where n is from 2 to 10;

or



5

where alkyl is  $-\text{O}-\text{CO}-(\text{CH}_2)_n-\text{CO}-\text{O}-$ , where  $n$  is from 2 to 10;



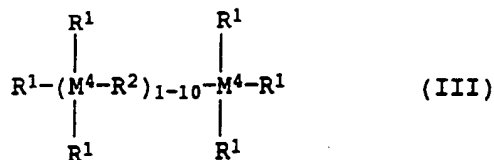
5

where

$\text{M}^3$  is a trivalent metal, such as Al or Y, and

$\text{R}^1$  and  $\text{R}^2$  are as defined above;

10

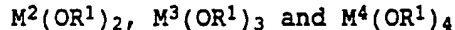


15

where  $\text{M}^4$  is a tetravalent metal, such as Sn(IV), Ti, Pb or Zr, and

$\text{R}^1$  and  $\text{R}^2$  are as defined above.

20 The polyfunctional initiators according to the invention are readily accessible by reacting the corresponding simple metal alkoxides



25

in a desired molar ratio with dialcohols or dicarboxylic acids in the presence or absence of high-boiling solvents, and removing the relatively high-volatility monohydric alcohol  $\text{R}^1\text{OH}$  by distillation.

30

It is also possible to react, under anhydrous conditions, a halide of the metals with the corresponding monoalcohol/diol mixture or with the corresponding monocarboxylic acid/dicarboxylic acid mixture with elimination of hydrogen chloride, and to scavenge the hydrogen chloride formed by addition of base.

In a particularly advantageous procedure, the monoalcohol/diol mixture or monocarboxylic acid/dicarboxylic acid mixture is introduced into a polar solvent, such as tetrahydrofuran, dioxane or diethylene glycol dimethyl ether, and the equivalent amount of metal halide, likewise dissolved in a polar solvent, is gradually added. A base, preferably a trialkylamine, is subsequently added, and the solution is separated from precipitated ammonium salt. After further dilution, if necessary, the solution can be employed as such as initiator solution.



It is advantageous to react Sn(II) carboxylates with relatively long-chain dicarboxylic acids with removal of the monocarboxylic acids by distillation to give the initiators according to the invention. Thus, for example, Sn(II) 2-ethylhexylcarboxylate or  
 5 Sn(II) octanoate is reacted at from 130 to 200°C with the corresponding amounts of dicarboxylic acids, for example adipic acid or dodecanedioic acid, where the molar ratio between Sn(II) monocarboxylate and dicarboxylic acid can be from 2:1 to 2:1.9, particularly advantageously from 2:1.5 to 2:1.6.

10

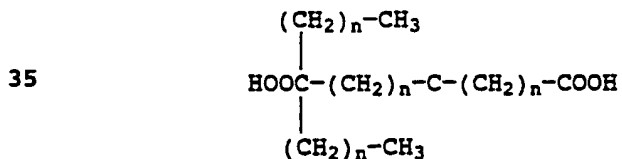
A very particularly preferred procedure is carried out without solvents and auxiliaries. Thus, polyfunctional Sn(II) carboxylates are prepared by, for example, reacting Sn(II) ethylhexanoic acid dicarboxylate directly with a difunctional or trifunctional  
 15 carboxylic acid at from 130 to 180°C under N<sub>2</sub>, and removing the ethylhexanoic acid liberated during this reaction by distillation, if necessary under reduced pressure.

In order to ensure high solubility of the polyfunctional initiators, the radicals R<sup>2</sup> should be as long as possible and crosslinking should be avoided. Preferred diols HO-R<sup>2</sup>-OH are 1,4-butanediol and 1,6-hexanediol. The preferred dicarboxylic acid HOOC-R<sup>2</sup>-COOH is adipic acid.

25 Very particularly preferred dicarboxylic acids are polyetherdicarboxylic acids of the type



30 having molecular weights of from 250 to 1000 g/mol, and commercially available dimeric fatty acids of the formula



35 having molecular weights of about 700 g/mol.

40

A particularly highly suitable tricarboxylic acid has a molecular weight of about 1000 g/mol and is prepared by trimerization of unsaturated fatty acids.

45 If the lactide polymerization is carried out with a mixture of monofunctional, bifunctional, trifunctional, etc., initiators in a stirred batch reactor or exclusively in a flow tube, molecular

weight distributions having a high content of relatively high-molecular-weight material are obtained.

By employing the novel initiators in accordance with the invention, any industrially relevant molecular weight distribution can be produced on an industrial scale.

#### Examples

10 The molecular weights of the polylactide samples prepared were determined by GPC. The inherent viscosity was measured at 25°C on a 0.1% strength solution in chloroform as solvent. The unit of inherent viscosity is 100 ml/g.

#### 15 Example 1

144 g (1 mol) of L-lactide are introduced into an argon-filled stirred flask and melted at 120°C. A solution of Sn(II) octanoate in toluene is then added by means of a syringe, the total amount  
20 of Sn(II) octanoate being  $10^{-4}$  mol. The  $10^{-4}$  mol of Sn(II) octanoate initiator is divided equally amongst four addition times, portions being metered in on the commencement of the polymerization, after 15 minutes, after 30 minutes and after 45 minutes. The polymerization is terminated after 60 minutes. The inherent  
25 viscosity is 1.19, the number average molecular weight is 44,000 and the weight average molecular weight is 140,000. The molecular weight distribution is virtually the same as Fig. 2, curve 5, and thus virtually corresponds to the relative molecular weight distribution obtained from Example 2. Compared with the comparative  
30 experiments, it has a significantly increased proportion of polymers of low molecular weight.

#### Example 2 (corresponding to variant B according to the invention)

35 Liquid L-lactide at 120°C is metered under pressure into a stirred reactor having a capacity of 5 l via a metering pump at a flow rate of 3 kg/h, corresponding to 20.8 mol/h. The reactor is kept under an argon blanket. The pressure is 4.5 bar and corresponds to the pressure necessary to force a corresponding flow rate  
40 through a nozzle in the base of the reactor. The polylactide extrudate formed is passed through a water bath, where it is quenched to give amorphous material and is then granulated.  $20.8 \cdot 10^{-5}$  mol/h of Sn(II) octanoate as a 1% strength solution in toluene are then metered in by means of a second metering pump.  
45 The reaction temperature is 190°C. The mean residence time for a fill level of 60% is about 1 hour. The granules are dried at 100°C, during which the small amount of toluene from the catalyst

solution is also removed. The inherent viscosity is 1.25, the number average molecular weight is 55,000 and the weight average molecular weight is 170,000. The molecular weight distribution is shown in Fig. 2, curve 5. The proportion by weight of molecular weights below 15% of  $M_w$  is 13%.

Example 3 (corresponding to variant B according to the invention)

The apparatus of variant A is supplemented by a flow tube having a volume of about 600 ml, a length of 58 cm and a diameter of 3.6 cm downstream of the stirred reactor. The flow tube and the reactor are heated to 190°C. 3 kg/h of L-lactide and  $20.8 \cdot 10^{-5}$  mol/h of Sn(II) octanoate are metered in as in Example 2. The mean residence time in the reactor is about one hour, and the mean residence time in the flow tube is about 12 minutes. the polymer melt is discharged through a nozzle at the end of the flow tube and passed through a water bath, and the amorphous extrudate is granulated. After drying, the inherent viscosity is 1.28, the number average molecular weight is 60,000 and the weight average molecular weight is 210,000. The molecular weight distribution is shown in Fig. 2, curve 6. The proportion by weight of molecular weights below 15% of  $M_w$  is 10%. Compared with variant A, however, the molecular weight distribution as a whole is shifted toward higher molecular weights.

25

Example 4 (corresponding to variant B according to the invention)

The last example is repeated but with the initiator metering divided.  $10.5 \cdot 10^{-5}$  mol/h of Sn(II) octanoate are metered into the stirred reactor, and  $10.5 \cdot 10^{-5}$  mol/h are again metered into the flow tube. After the granules have been dried, the inherent viscosity is 1.20, the number average molecular weight is 63,000 and the weight average molecular weight is 280,000. The molecular weight distribution is shown in Fig. 2, curve 7. The proportion by weight of molecular weights below 15% of  $M_n$  is 14%.

Example 5 (corresponding to variant C according to the invention)

40

The polymerization is carried out in two twin-walled flow tubes connected in series and fitted with static mixing elements for better mixing of the melt. 3 kg/h of L-lactide are metered into the first flow tube at 180°C, and  $20.8 \cdot 10^{-5}$  mol/h of Sn(II) octanoate as a 1% strength solution in toluene are metered in via a second metering pump. The melt temperature is held at 190°C. At the end of the first flow tube, the melt is fed back to the

beginning of the tube at a flow rate of about 15 l/h via a gear pump likewise heated to 190°C, where it is mixed with fresh monomer and initiator. 3 kg/h are force-conveyed into the second flow tube. The melt is then discharged through a nozzle at the end of the second flow tube and cooled in the water bath, and the amorphous extrudate is granulated. The mean residence time in the first flow tube is about 30 minutes and that in the second flow tube is about 15 minutes. After drying, the inherent viscosity is 1.14, and the number average molecular weight is 52,000. The molecular weight distribution is shown approximately in Fig. 2, curve 6. The proportion by weight of molecular weights below 15% of  $M_n$  is 11%.

Example 6 (corresponding to variant C according to the invention)

15

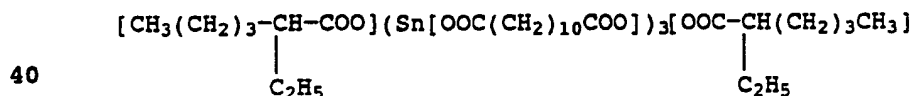
Example 5 is repeated, but with divided initiator metering.  $10.5 \cdot 10^{-5}$  mol/h of Sn(II) octanoate are metered into the first flow tube, and a further  $10.5 \cdot 10^{-5}$  mol/h are metered into the second flow tube. After the granules have been dried, the inherent viscosity is 1.22, the number average molecular weight is 75,000 and the weight average molecular weight is 410,000. Compared with undivided initiator metering, the molecular weight distribution is essentially broader. The molecular weight distribution is shown approximately in Fig. 2, curve 7.

25

Example 7 (polymerization using polyfunctional catalyst)

a) Preparation of the polyfunctional catalyst

30 15.07 g, corresponding to 0.037 mol, of Sn(II) 2-ethylhexanoate are melted in a flask under nitrogen together with 6.45 g, corresponding to 0.028 mol, of 1,10-dodecanedioic acid, and 7.1 g (theory 8.064 g) of 2-ethylhexanoic acid are removed by distillation at 150°C in a stream of nitrogen. the reaction mixture comprises an oligomer mixture having the mean composition



45 It dissolves in a concentration of 2% in 1,2-dichlorobenzene at about 100°C. The solution becomes somewhat cloudy on cooling.

## b) Polymerization

144 g (1 mol) of L-lactide are introduced into an argon-filled stirred flask and melted at 120°C. The initiator solution is then added by means of a syringe. The initiator solution comprises 1,2-dichlorobenzene as solvent, and the total amount of initiator is about 1%. The solution contains  $0.8 \cdot 10^{-5}$  mol of Sn(II) 2-ethylhexanoate and  $0.2 \cdot 10^{-5}$  mol of the catalyst, based on the tin. After heating to 190°C, the polymerization is commenced. After 45 minutes, the polymerization is terminated. The inherent viscosity is 1.31 100 ml/g. The molecular weight distribution has a bimodal character with a weight average molecular weight peak at 260,000 and a secondary peak of about 9% of the proportion by weight between 700,000 and 2,000,000. The relative frequency is shown in Fig. 1, curve 3.

## Comparative Example 1

144 g (1 mol) of L-lactide are introduced into an argon-filled stirred flask and melted at 120°C. A solution of Sn(II) octanoate in toluene is then added by means of a syringe, the amount of Sn(II) octanoate being  $10^{-4}$  mol. Heating is then continued, and the polymerization is carried out at 180°C. After 60 minutes, the inherent viscosity is 1.34, the number average molecular weight is 74,000 and the weight average molecular weight is 210,000. The molecular weight distribution is shown in Figs. 1 and 2.

## Comparative Example 2

Comparative Example 1 is repeated with  $10^{-5}$  mol of initiator. After a reaction time of 75 minutes at 220°C, the inherent viscosity is 0.69, the number average molecular weight is 48,000 and the weight average molecular weight is 97,000. The molecular weight distribution is shown in Figs. 1 and 2.

## Comparative Example 3

Comparative Example 1 is repeated with  $5 \cdot 10^{-5}$  mol of initiator. After a reaction time of 75 minutes at 180°C, the intrinsic viscosity is 1.40, the number average molecular weight is 72,000 and the weight average molecular weight is 230,000. The molecular weight distribution is shown in Figs. 1 and 2.

CLAIMS

1. A polylactide having a number average molecular weight of greater than 30,000 or a weight average molecular weight of greater than 60,000, wherein the proportion by weight in the molecular weight range up to 10,000 and in the molecular weight range above 500,000 is in each case from 5 to 15%.
2. A process for the preparation of a polylactide as claimed in claim 1 by polymerisation of a lactide in the presence of an initiator wherein the initiator is added in a plurality of portions at different times and/or, if the process is carried out continuously, at a plurality of consecutive locations.
3. A process for the preparation of a polylactide as claimed in claim 1 by polymerisation of a lactide in the presence of an initiator, wherein both a monofunctional initiator and a polyfunctional initiator are used.
4. A process for the preparation of a polylactide as claimed in claim 1 by polymerisation of a lactide, wherein the polymerisation is carried out in a continuous stirred reactor.
5. A process for the preparation of a polylactide as claimed in claim 1 by polymerisation of a lactide, wherein the polymerisation is carried out in part in a continuous stirred reactor, downstream of which is a reactor with plug flow in which the polymerisation is completed.
6. A process for the preparation of a polylactide as claimed in claim 1 carried out substantially as hereinbefore described or illustrated in any of the foregoing Examples 1 to 7.

7. Packaging material comprising polylactide as claimed in claim 1 or polylactide prepared by a process as claimed in any of claims 2 to 6.